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A theoretical study of cyanide on alkali-halide and alkali-metal surfaces using density functional theory

by

Jason P. Modisette

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE Master of Arts

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Houston, Texas
May, 1995
Abstract

A theoretical study of cyanide on alkali-halide and alkali-metal surfaces using density functional theory

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Jason P. Modisette

Many interesting physical phenomena have been observed in electron-stimulated desorption studies of the cyanide molecule on alkali halide and alkali metal surfaces. We have performed a theoretical investigation of the nature of the cyanide-surface bond and of the desorption process using an \emph{ab initio} density functional theoretic method of calculating electronic structure in the local density and Born-Oppenheimer approximations. We compare our results with experiment, and offer an explanation for an anomalous non-Boltzmann, temperature-independent rotational distribution experimentally observed in cyanide desorbed from these surfaces. As a verification of the method, we have performed extensive calculations on different bare alkali halide and alkali metal clusters and compared them with experimental results.
Acknowledgments

I would like to thank Liang Lou for providing the CMOL method used in this research and for his valuable explanations of the theory and techniques on which it is based. My advisor, Peter Nordlander, has been very helpful in discussing all of the work contained here, and in elucidating the physics behind these results. I appreciate the time and effort spent by the other members of my thesis committee, King Walters and Barry Dunning, in reading the thesis and participating in its oral defense. I would also like to thank the Robert A. Welch Foundation for their support of this research.
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Chapter 1

Introduction

Alkali halides are fundamentally interesting as simple systems that exhibit an ionic bond. From a technological perspective, alkali halides are of considerable importance as insulators and as optical materials [1, 2]. Recently, the interest in these materials has grown as experiments have shown that alkali halide surfaces can exhibit a wide range of important desorption and sputtering phenomena [3, 4, 5]. Many gas phase electron diffraction studies have been performed on alkali halide clusters, so there theoretical models of these systems can be verified against a wide range of experimental data [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17].

One interesting, unexplained experimental result in this field occurs during electron-stimulated desorption (ESD) of several species of diatomic molecules from alkali halide surfaces. The simplest system exhibiting this behavior is cyanide adsorbed on a lithium fluoride surface. The emitted cyanide molecules populate excited rotational quantum states in a non-Boltzmann distribution which is independent of substrate temperature and beam energy [18]. This anomalous distribution of rotational excitations has since been observed in cyanide emitted from many other alkali halide and alkali metal surfaces [19], as well as other diatomic molecules desorbed from metal and metal oxide surfaces [20, 21]. The cyanide emitted from these systems was first detected by its optical emission as it underwent the transition from the $B^2\Sigma^+$ to the $X^2\Sigma^+$ molecular electronic state. The electronic excitation of the emitted cyanide is strong evidence that a desorption induced by electronic transition (DIET) is occurring. DIET processes can produce a rich variety of physical effects, and their study is currently a very active topic in surface research [22, 23]. The theory of
DIET combined with ESD experiments promises to be a powerful tool for examining adsorbate-surface interactions.

Several explanations have been proposed for the non-Boltzmann distribution of rotational states [24, 25, 21]. None of these have been verified by accurate theoretical \textit{ab initio} calculations. Molecular dynamics methods have been proposed to accurately model DIET processes, but they also require accurate \textit{ab initio} potential surfaces [26, 27, 28]. The generation of these potentials requires a theory that correctly represents alkali halides, alkali metals, and the ground and excited states of cyanide that are involved in the desorption process. We find that our all-electron local density method, described in Chapter 2, is very accurate for all of these systems, while sufficiently computationally efficient to model the large clusters that may be required to represent surfaces.

The theoretical modeling of alkali halides is computationally challenging. For a proper description of the electronic structure of ionic systems, it is crucial to represent the Coulomb potential accurately. There are cusps in the Coulomb potential at the atomic nuclei which cause cusps in the electronic wavefunctions. These wavefunctions are difficult to represent with a small basis set unless the basis functions are carefully chosen. Also, in the modeling of bulk and surface structures the long range of the Coulomb potential makes it necessary to incorporate a large number of atoms, while still accurately representing exchange and correlation effects. For many metallic and covalent systems, the local density approximation (LDA) proves to be fast and accurate for electronic structure calculations and therefore provides a preferred option to more elaborate \textit{ab initio} techniques, such as configuration interaction [2]. Less is known about the LDA for small ionic systems. The two goals of this thesis are to investigate the accuracy of the LDA for these alkali halide and alkali metal systems and the relevant states of cyanide, and to generate accurate ground- and excited-
state potentials for cyanide on the surfaces of interest with the aim of explaining the anomalous rotational state population that has been observed.

We begin by investigating the accuracy of our method for the relevant molecules and clusters. We calculate many physical properties of alkali halide and alkali metal monomers and dimers for comparison with experimental gas-phase electron diffraction results. We find that the calculated properties are in excellent agreement with experimental values, and have accuracies comparable with more elaborate theoretical calculations. Our calculated LDA values for the bond lengths, vibrational modes, anharmonicities, and binding energies of the $X^2Σ^+$ ground state and $B^2Σ^+$ excited state of the cyanide molecule are also in very good agreement with most experimental data.

We find that there is an excited electronic state of cyanide on the alkali halide and alkali metal surfaces we have examined which derives from the $B^2Σ^+$ state of free cyanide. Having identified this surface electronic state, we can generate a potential for the combined excited state of cyanide and the surface which is the state involved in the DIET of these molecules. We calculate the potential energy surface for both the ground and excited states of cyanide on clusters chosen to optimally represent the lithium metal (100) surface. We compare these potentials with the free-rotor and hindered-rotor model potentials that have been suggested to explain the anomalous rotational distributions of emitted cyanide [21, 29, 20], and find that some of the proposed model potentials are in qualitative agreement with our ab initio calculations.

We will begin by discussing the details of CMOL, the theoretical method, in chapter II of this thesis. In chapter III, we present the calculated equilibrium properties for alkali halide and alkali metal monomers and dimers, and compare them with experimental values and with the results of other ab initio theoretical approaches. We will also discuss our findings concerning the source of unexplained absorption lines that were previously suspected to come from a linear form of the lithium fluoride
dimer. Our calculations for potassium and potassium halide clusters show significantly larger deviations from experiment than the other systems we have examined, indicating that more accurate theoretical methods may be necessary. We examine the effects on potassium halide electronic structure of extending the LDA to include empirical forms of the non-local exchange and correlation potentials. In chapter IV, we compare our theoretical results for the bonding of cyanide to lithium and lithium fluoride surfaces with several different experiments, and show that our theoretical potential energy surfaces explain the rotational excitation of emitted cyanide as well as the correspondence that has been seen between the degree of metallization of an alkali halide surface and the cyanide yield.

Since the beam electrons in ESD experiments transfer energy to cause the excitation, one expects to see a desorption threshold at an electron energy corresponding to the excitation. This experiment has been performed for cyanide desorbed from potassium metal, a system which exhibits a similar surface-temperature-independent rotational distribution to that seen on lithium fluoride. We compare this experimental threshold with our results for cyanide on potassium metal, and make predictions for its value on lithium metal and lithium fluoride surfaces.
Chapter 2

The theoretical method

2.1 Density functional theory

Density functional theory is based on a theorem of Hohenberg and Kohn that all
properties of the ground state of an electronic system are functionals of only the
charge density, and not of the electronic wavefunctions except as they contribute to
the charge density. Minimizing the energy of a system with respect to the density with
the constraint that there be a fixed number of electrons leads to an Euler equation for
this ground-state electronic density. Kohn and Sham showed that a noninteracting
one-electron Hamiltonian with a modified external potential can be constructed to
give the same ground state density as the true interacting problem, and therefore
to give all other ground-state properties [30, 31, 32]. By solving only this noninter-
acting Hamiltonian, the ground-state density is obtained with computational effort
considerably reduced from that required to solve the full problem. This formalism
is also valid for the certain excited states, i.e. the lowest-energy electronic state of
each symmetry. The effective potential in the Kohn-Sham Hamiltonian depends on
the density, so its solution must be iterated until self-consistency is achieved, which
is when the density given by the eigenvectors of the Hamiltonian is the same as the
density used to generate the effective potential.

2.2 The local density approximation

Electron-electron interactions are included exactly in the Kohn-Sham Hamiltonian
as terms in the effective one-electron local potential. The time-averaged electronic
Coulomb interaction is written exactly as a functional of the density, but exact ex-
pressions for exchange and correlation are not available. This exact expression would be a functional of the electronic density over all space. One of the most successful approximate exchange-correlation potentials is the local density approximation (LDA), which replaces the exact exchange-correlation functional with a local function of the density. The LDA exchange-correlation potential is equal to the exchange-correlation energy per particle of a free electron gas with a density and spin density equal to the local values. The LDA has been successfully applied to a variety of atomic and molecular systems [33, 34]. In the present calculation, the von Barth-Hedin parameterization of the local exchange-correlation potential has been used [35]. The LDA does not properly account for correlation effects in regions of low electronic density, but in the case of alkali halide systems correlation has been found to have little effect on the geometries [36].

2.3 CMOL

The method used in this work for solving the Kohn-Sham equations is the CMOL program, written by Liang Lou [33]. In this approach, the one-particle wavefunctions are expanded in a basis of numerically tabulated atomic orbitals. These basis functions are the radial wavefunctions from numerical LDA solutions of free atoms and molecules in the central field approximation combined with spherical harmonics. The basis sets include the appropriate numerical atomic orbital for each electron, and in addition the 2+ ionic numerical orbital for each valence electron. This basis set has been shown to perform very well in LDA electronic structure calculations of molecules and a wide range of cluster systems [37].

The Coulomb potential is obtained directly by solving Poisson's equation using an expansion of the charge density in spherical harmonics around each atomic center. The convergence of this expansion at different atomic centers is facilitated by
the use of partitioning functions which decompose the charge density into atom-like components, so that quadratures developed specifically for the atomic problem can be applied. This integration method is similar to those used by Becke [38] and Delley [37].
Chapter 3

Results for alkali and alkali halide clusters

3.1 Alkali halide clusters

3.1.1 Monomers

The properties of alkali halide monomers are experimentally well known. We have calculated the equilibrium bond lengths, vibrational frequencies, anharmonicities, and binding energies for the monomers of lithium, sodium, and potassium with fluorine, chlorine, and bromine. The results are presented in Table 3.1, together with experi-

Table 3.1 Equilibrium properties of alkali halide monomers. Bond lengths $d$ are given in Å, vibrational frequencies and anharmonicities $\omega$ and $\chi\omega$ in cm$^{-1}$. Present results are indicated by LDA, restricted Hartree-Fock results (from [36]) by RHF, and experimental data (from [17]) by exp.

<table>
<thead>
<tr>
<th></th>
<th>$d^{LDA}$</th>
<th>$d^{RHF}$</th>
<th>$d^{exp}$</th>
<th>$\omega^{LDA}$</th>
<th>$\omega^{RHF}$</th>
<th>$\omega^{exp}$</th>
<th>$\chi\omega^{LDA}$</th>
<th>$\chi\omega^{exp}$</th>
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<td>1.551</td>
<td>1.565</td>
<td>1.564</td>
<td>915</td>
<td>937</td>
<td>910</td>
<td>7.5</td>
<td>7.9</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.004</td>
<td>2.041</td>
<td>2.021</td>
<td>640</td>
<td>639</td>
<td>643</td>
<td>6.8</td>
<td>4.5</td>
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<tr>
<td>LiBr</td>
<td>2.150</td>
<td>2.170</td>
<td>566</td>
<td>563</td>
<td>563</td>
<td>5.3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>1.916</td>
<td>1.923</td>
<td>1.926</td>
<td>541</td>
<td>545</td>
<td>536</td>
<td>5.4</td>
<td>2.4</td>
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<td>NaCl</td>
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<td>2.400</td>
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<td>353</td>
<td>366</td>
<td>2.6</td>
<td>2.0</td>
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<td>NaBr</td>
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<td>2.502</td>
<td>306</td>
<td>302</td>
<td>302</td>
<td>1.7</td>
<td>1.5</td>
<td></td>
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<tr>
<td>KF</td>
<td>2.103</td>
<td>2.238</td>
<td>2.171</td>
<td>467</td>
<td>413</td>
<td>428</td>
<td>3.1</td>
<td>2.4</td>
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<tr>
<td>KCl</td>
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<td>2.779</td>
<td>2.667</td>
<td>300</td>
<td>259</td>
<td>281</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>KBr</td>
<td>2.753</td>
<td>2.821</td>
<td>232</td>
<td>213</td>
<td>213</td>
<td>1.0</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

imental data and results from another recent theoretical study. For the lithium and sodium monomers, the bond lengths in are within 0.03 Å of experimental values. For the potassium monomers, the agreement is within 0.07 Å. The monomer equilibrium geometries were determined by finding the zero-gradient point, rather than the minimum-energy geometry, for the sake of consistency with other calculations.
As argued by Pulay [39], the force constants of a molecule should be determined by a single numerical differentiation of analytical energy gradients. This procedure eliminates the errors associated with an extra numerical differentiation of total energy as a function of intramolecular bond lengths. To be consistent, we used this approach to determine the vibrational frequencies of the monomers as well as the dimers, which will be described below. For the monomers, we obtained vibrational frequencies and anharmonicities by fitting the analytically generated energy gradients to a Morse potential. We found that the shape of the calculated potential matched the Morse potential very closely in the region near the potential minimum. The calculated monomer vibrational frequencies are all within 1% of the experimental values for the lithium and sodium halides, and consistently about 10% too high for the potassium halides. In all of the monomers, the calculated bond lengths were too short and the calculated vibrational frequencies too high. The errors in vibration frequency are roughly proportional to the errors in bond length, and are worst in the potassium halides. We believe that these systematic discrepancies are signs of a small effect due to non-local exchange and correlation, which are not included in the LDA.

As a check of the method, we fitted the energies rather than the gradients to a Morse potential. We found that this typically doubled the disagreement with experimental values, and also that there were no visible trends in the direction of the deviation from experiment. We believe that this confirms that using the energies rather than the gradients in calculating force constants leads to increased numerical errors. We will use the only the analytical gradients for the calculations of vibrational frequencies and anharmonicities in the remainder of this work.
3.1.2 Dimers

It is generally accepted that the equilibrium geometries of alkali halide dimers are planar rings with $D_{2h}$ symmetry. Extensive gas-phase electron diffraction studies have been performed on these systems, so experimental bond angles and lengths are available [6, 7, 9, 10, 11, 40]. We have calculated the equilibrium geometries by determining the zero-gradient point, as was done with the monomers. The results are presented in Table 3.2 together with experimental results and data from a recent theoretical study. It can be seen that the calculated bond lengths compare very well with

<table>
<thead>
<tr>
<th></th>
<th>$d^{LDA}$</th>
<th>$d^{exp}$</th>
<th>$d^{RHF}$</th>
<th>$\theta^{LDA}$</th>
<th>$\theta^{exp}$</th>
<th>$\theta^{RHF}$</th>
<th>Ref.</th>
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<td>Li$_2$F$_2$</td>
<td>1.699</td>
<td>1.746 ± 0.015</td>
<td>1.717</td>
<td>100.0</td>
<td>104.7 ± 2.3</td>
<td>99.5</td>
<td>[6]</td>
</tr>
<tr>
<td>Li$_2$Cl$_2$</td>
<td>2.170</td>
<td>2.23 ± 0.03</td>
<td>2.222</td>
<td>107.9</td>
<td>108 ± 4</td>
<td>107.5</td>
<td>[7]</td>
</tr>
<tr>
<td>Li$_2$Br$_2$</td>
<td>2.325</td>
<td>2.35</td>
<td></td>
<td>110.4</td>
<td>110 ± 4</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>Na$_2$F$_2$</td>
<td>2.047</td>
<td>2.121 ± 0.005</td>
<td>2.065</td>
<td>94.8</td>
<td>96.0 ± 3.0</td>
<td>93.1</td>
<td>[9]</td>
</tr>
<tr>
<td>Na$_2$Cl$_2$</td>
<td>2.500</td>
<td>2.584 ± 0.034</td>
<td>2.574</td>
<td>102.8</td>
<td>101.4 ± 2.4</td>
<td>100.8</td>
<td>[10]</td>
</tr>
<tr>
<td>Na$_2$Br$_2$</td>
<td>2.644</td>
<td>2.740 ± 0.034</td>
<td></td>
<td>105.2</td>
<td>101.6 ± 1.8</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>K$_2$F$_2$</td>
<td>2.291</td>
<td>2.347 ± 0.028</td>
<td>2.416</td>
<td>85.6</td>
<td>84.7 ± 1.6</td>
<td>85.6</td>
<td>[9]</td>
</tr>
<tr>
<td>K$_2$Cl$_2$</td>
<td>2.787</td>
<td>2.950 ± 0.054</td>
<td>2.970</td>
<td>93.7</td>
<td>96.0 ± 2.4</td>
<td>92.3</td>
<td>[10]</td>
</tr>
<tr>
<td>K$_2$Br$_2$</td>
<td>2.942</td>
<td>3.202 ± 0.022</td>
<td></td>
<td>96.6</td>
<td>95.8 ± 1.4</td>
<td></td>
<td>[11]</td>
</tr>
</tbody>
</table>

Table 3.2 Equilibrium properties of alkali halide rhombic dimers. Bond lengths $d$ are given in Angstroms, opening angles $\theta$ in degrees. Present results are indicated by $LDA$, restricted Hartree-Fock results (from [36]) by $RHF$, and experimental data by $exp$. The references for experimental data are also listed.

experiment, and that the opening angles agree with the measured values to within a few degrees, which is the same order as the experimental uncertainty. The calculated dimer bond lengths are consistently about 0.05 Å shorter than experimental values. This follows the trend seen in the monomers.

The dimerization energy is the energy needed to separate a dimer into two identical monomers. Experimental values for the dimerization energy are known for most of the
systems we have examined here [12, 41, 42, 43, 44, 45]. The calculated dimerization energies are listed in Table 3.3. For lithium halides, the calculated energies are all within 5% of experimental values. The calculated dimerization energies of the sodium halides are about 10% higher than the experimental values. For the potassium-containing dimers, the calculated energies are as much as 30% too high.

Table 3.3 Energies of dimerization of alkali halides. All energies \( E_D \) are given in eV. Present results are indicated by \( LDA \), restricted Hartree-Fock results (from [36]) by \( RHF \), and experimental data by \( \text{exp}^* \).

<table>
<thead>
<tr>
<th></th>
<th>( E_D^{LDA} )</th>
<th>( E_D^{RHF} )</th>
<th>( E_D^{\text{exp}} )</th>
</tr>
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<tr>
<td>Li(_2)F(_2)</td>
<td>2.80</td>
<td>2.73</td>
<td>2.76</td>
</tr>
<tr>
<td>Li(_2)Cl(_2)</td>
<td>2.24</td>
<td>2.07</td>
<td>2.36</td>
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<td>Li(_2)Br(_2)</td>
<td>2.07</td>
<td>2.14</td>
<td>2.14</td>
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<tr>
<td>Na(_2)F(_2)</td>
<td>2.85</td>
<td>2.62</td>
<td>2.57</td>
</tr>
<tr>
<td>Na(_2)Cl(_2)</td>
<td>2.07</td>
<td>2.02</td>
<td>2.24</td>
</tr>
<tr>
<td>Na(_2)Br(_2)</td>
<td>1.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)F(_2)</td>
<td>2.85</td>
<td>2.20</td>
<td>2.14</td>
</tr>
<tr>
<td>K(_2)Cl(_2)</td>
<td>2.33</td>
<td>1.85</td>
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<tr>
<td>K(_2)Br(_2)</td>
<td>2.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Table 3.4 we present calculated vibrational frequencies for the dimers. Only the IR-active modes are shown, since no experimental data are available for the frequencies of other modes. The force constants are determined from the analytical energy gradients calculated at small displacements from equilibrium.

The experimental data available on the vibrational frequencies of the alkali halide dimers are incomplete, and in several cases the experimental values are in disagreement. Alkali halide clusters will form bulk material if allowed to crystallize. The vibrational spectra for these systems have therefore been obtained by trapping them in a solid noble gas matrix. The effects of the adjacent matrix atoms on the properties of the cluster are believed to be small in most cases, but are not well understood.

Snelson [46] has proposed an empirical method, which we have used, for determining
Table 3.4 Vibrational frequencies of the rhombic dimer, listed by mode. All frequencies are in cm⁻¹. Only the IR-active modes are shown here. "Li indicates a mixture of ⁶Li and ⁷Li at natural abundances. Present results are indicated by LDA, restricted Hartree-Fock results (from [36]) by RHF, and experimental data by exp. These experimental data are taken from [13, 14, 15, 47, 16]

<table>
<thead>
<tr>
<th></th>
<th>B_{1u}^{LDA}</th>
<th>B_{1u}^{RHF}</th>
<th>B_{1u}^{exp}</th>
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<th>B_{2u}^{RHF}</th>
<th>B_{2u}^{exp}</th>
<th>B_{3u}^{LDA}</th>
<th>B_{3u}^{RHF}</th>
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<td>^nLi₂F₂</td>
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<td>305</td>
<td>596</td>
<td>600</td>
<td>550</td>
<td>697</td>
<td>698</td>
<td>640</td>
<td></td>
</tr>
<tr>
<td>^nLi₂F₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>^6Li₂F₂</td>
<td>306</td>
<td>320</td>
<td>629</td>
<td>600</td>
<td>735</td>
<td>695</td>
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<tr>
<td>^7Li₂F₂</td>
<td>289</td>
<td>300</td>
<td>594</td>
<td>570</td>
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<td>374</td>
<td>380</td>
<td>536</td>
<td>513</td>
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<tr>
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</tr>
<tr>
<td>^nLi₂Br₂</td>
<td>137</td>
<td>162</td>
<td>149</td>
<td>383</td>
<td>383</td>
<td>369</td>
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<td>^nLi₂Br₂</td>
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<td>369</td>
<td>411</td>
<td>394</td>
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<tr>
<td>Na₂F₂</td>
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<td>Na₂Cl₂</td>
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<td>96</td>
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<td>244</td>
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<td>Na₂Br₂</td>
<td>70</td>
<td>106</td>
<td>197</td>
<td>186</td>
<td>251</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

free space vibrational frequencies of alkali halide clusters from measured neon matrix isolation frequencies. This method is believed to introduce an error of 15 cm⁻¹ to the experimental data. All of the experimental frequencies in Table 3.4 are gas-phase-corrected values from neon matrix-isolation spectra, except for the data for Na₂F₂, Na₂Cl₂, and Na₂Br₂ [47], which were made in an argon matrix. The calculated frequencies are in very good agreement with the limited experimental data.

Neon matrix isolation studies have been performed on the C_{2v} structure of the mixed dimer LiNaF₂, which has six IR-active modes [16]. In Table 3.5, we present our calculated vibrational frequencies for this system. All vibrational frequencies, with the exception of one of the B₂ modes, are within 10% of the experimental values.
Table 3.5  Vibrational frequencies of the planar cyclic cluster LiNaF₂, listed by mode. Present results are indicated by LDA, experimental data (from [16]) by exp.

<table>
<thead>
<tr>
<th></th>
<th>A₁</th>
<th>A₁</th>
<th>A₁</th>
<th>B₂</th>
<th>B₂</th>
<th>B₁</th>
</tr>
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<tbody>
<tr>
<td>LDA</td>
<td>669</td>
<td>408</td>
<td>295</td>
<td>772</td>
<td>357</td>
<td>255</td>
</tr>
<tr>
<td>exp</td>
<td>600</td>
<td>377</td>
<td>621</td>
<td>327</td>
<td>249</td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>631</td>
<td>408</td>
<td>292</td>
<td>727</td>
<td>357</td>
<td>244</td>
</tr>
<tr>
<td>exp</td>
<td>660</td>
<td>376</td>
<td>589</td>
<td>326</td>
<td>238</td>
<td></td>
</tr>
</tbody>
</table>

3.1.3 Linear dimers

Redington and others have argued that certain bands in the matrix isolation spectra of lithium fluoride could be due to a different form of the dimer, with two inequivalent lithium sites[48, 49]. They proposed a matrix-stabilized linear dimer to explain these bands. Our calculations show that in free space, a linear dimer is only 0.03 eV less stable than the rhombic form. A normal mode analysis of linear Li₂F₂ yielded high-frequency stretching modes at 929 and 854 cm⁻¹, while the unexplained peaks seen by Redington were at 737 and 511 cm⁻¹. This indicates that these peaks are not due to the presence of a linear dimer, unless there is a much larger shift due to the matrix here than we have seen in any of the rhombic dimers.

3.1.4 Comparison with other ab initio theoretical results

Comparing the present results for the monomers with recent Hartree-Fock calculations [36], also shown in Table 3.1, the two methods clearly agree with each other and with experiment. While both sets of calculations show the poorest agreement with experiment for the potassium monomers and dimers, the Hartree-Fock bond lengths in these systems tend to be too large, while the present results underestimate the bond lengths by a similar amount. For the lithium and sodium monomers, the LDA
vibrational frequencies are closer to experiment that the results of [36], while for potassium both methods typically differ from experimental frequencies by at least 20 cm\(^{-1}\).

3.2 Alkali metal dimers

The yield of emitted cyanide from alkali halide surfaces has been observed to increase with increasing exposure time to the electron beam in ESD experiments [5]. It is known that the electron beam causes the formation of alkali metal islands on the surface [3]. A theoretical examination of the problem of the anomalous rotational excitation would not be complete without an investigation of the bonding of cyanide to alkali metal surfaces. The two metals that have been experimentally used for these ESD studies are lithium and potassium. To verify our method’s treatment of these materials, we calculated equilibrium properties of the Li\(_2\) and K\(_2\) dimers just as we did with the alkali halide monomers. These results are compared with experiment in Table 3.6. The duplication of experimental values is exceptionally good for these

<table>
<thead>
<tr>
<th></th>
<th>(r_e^{LDA})</th>
<th>(r_e^{\text{expt}})</th>
<th>(\omega_e^{LDA})</th>
<th>(\omega_e^{\text{expt}})</th>
<th>(\chi_e^{LDA})</th>
<th>(\omega_e^{LDA})</th>
<th>(\chi_e^{\text{expt}})</th>
<th>(\omega_e^{\text{expt}})</th>
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</thead>
<tbody>
<tr>
<td>Li(_2)</td>
<td>2.72</td>
<td>2.6729</td>
<td>337.2</td>
<td>351.43</td>
<td>2.3</td>
<td>2.6100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)</td>
<td>3.84</td>
<td>3.9051</td>
<td>94.3</td>
<td>92.021</td>
<td>0.21</td>
<td>0.2829</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

systems. Bond lengths are reproduced to 2%, vibrational frequencies to 5%, and anharmonicities to 25% for both lithium and potassium. This shows that the LDA is adequate for an accurate description of these systems.
3.3 Other parameterizations of the LDA

The parameterization of the exchange and correlation energy functionals used in these calculations is that of von Barth and Hedin [35], which is based on the analytical solution of an approximation to the spin-polarized electron gas. Since the publication of this potential, Monte-Carlo simulations have been used to more exactly determine the correlation energy of the spin-polarized electron gas [50, 51]. Several correlation potentials have been published which parameterize these results [52, 53]. To verify the adequacy of this parameterization of the correlation energy, we have implemented the alternate functionals of Vosko, Wilk, and Nusair [52] and of Perdew and Zunger [53], which parameterize the results of [50, 51]. We find that the equilibrium bond lengths calculated with the new parameterizations never differ by more than 0.002 Å or the vibrational frequencies by more than 3 cm⁻¹ from the values obtained with the correlation energy of von Barth and Hedin. Variations of this size are insignificant compared to the differences with experiment. They are also much smaller than the changes caused by the introduction of a non-local exchange potential, described in Section 3.4.

3.4 Non-local effects in potassium and potassium halides

The potassium monomer results are clearly significantly further from experimental values than those of the lithium and sodium halides. The potassium basis set did not contain orbitals for the neutral 3d, 4p, and 4d levels, which we thought might be significant contributors to the occupied molecular orbitals. We added these orbitals to the basis set, and although they did cause the bonds of all the potassium halides to expand by about 0.004 Å, this did not come close to the discrepancy with experiment. The inclusion of +4 ionic valence orbitals for chlorine in the KCl monomer had similar effects, expanding the bond length by 0.005 Å.
We examined the calculated bond lengths for K₂ and KH molecules, and found them to be too short in both systems by about 0.04 Å per potassium atom. This error is comparable to the error in the bond length for potassium halides, and seems to reflect a systematic underestimate of the spatial extent of the electron cloud of potassium. The calculated ionization potentials were 6%, 9%, and 10% too high for lithium, sodium, and potassium atoms, respectively. Since an ionization potential which is too high corresponds to an electron cloud which is too tight, the directions of these errors support an interpretation of the bond length errors as due to the incorrect representation of the size of the atomic alkali orbitals.

The exchange-correlation potential, as was discussed in Chapter 2 is approximated in the LDA as a local functional of the electronic density. This neglects effects such as the polarization potential which are due to nonlocal exchange and correlation. The polarizability of potassium is very large (43.4 Å³) compared to lithium (24.3 Å³) and sodium (23.6 Å³), so a more accurate expression than the LDA may be necessary to correctly model potassium-containing systems. In order to test this idea, calculations were performed using an approximation to this complete, non-local exchange potential. The semiempirical gradient correction of Becke [54], which reproduces the exact long-range behavior of the interaction of the electron with its exchange-correlation hole, was used. This nonlocal potential has performed very well in atomic calculations. In table 3.7, the bond lengths calculated with the inclusion of this nonlocal exchange correction are listed together with the LDA results and experimental data. This simple correction to the exchange potential of the LDA treatment resulted in significantly longer bonds for all species considered, with the greatest expansion in the potassium monomers. We believe this indicates that non-local effects are significant in the potassium halides when compared to the other systems, and should be included in any accurate calculation for these species. Further investigations using
more elaborate schemes for non-local corrections [55, 56] are required before this issue can be settled.

Table 3.7  The effects of nonlocal gradient-exchange corrections to the LDA on the bond lengths of alkali halide monomers. The uncorrected bond lengths, in Å, are listed by $d^{LDA}$, the bond lengths with the non-local correction by $d^{NL}$, and the experimental results by $d^{exp}$. The expansion of the bond with the inclusion of the non-local correction is also given.

<table>
<thead>
<tr>
<th></th>
<th>$d^{LDA}$</th>
<th>$d^{NL}$</th>
<th>$d^{exp}$</th>
<th>expansion</th>
</tr>
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<tr>
<td>LiF</td>
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<td>1.590</td>
<td>1.555</td>
<td>0.049</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.004</td>
<td>2.055</td>
<td>2.021</td>
<td>0.051</td>
</tr>
<tr>
<td>LiBr</td>
<td>2.150</td>
<td>2.221</td>
<td>2.170</td>
<td>0.071</td>
</tr>
<tr>
<td>NaF</td>
<td>1.916</td>
<td>1.965</td>
<td>1.926</td>
<td>0.049</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.338</td>
<td>2.373</td>
<td>2.361</td>
<td>0.045</td>
</tr>
<tr>
<td>NaBr</td>
<td>2.473</td>
<td>2.502</td>
<td>2.502</td>
<td>0.029</td>
</tr>
<tr>
<td>KF</td>
<td>2.103</td>
<td>2.184</td>
<td>2.171</td>
<td>0.079</td>
</tr>
<tr>
<td>KCl</td>
<td>2.601</td>
<td>2.683</td>
<td>2.667</td>
<td>0.082</td>
</tr>
<tr>
<td>KBr</td>
<td>2.753</td>
<td>2.824</td>
<td>2.821</td>
<td>0.081</td>
</tr>
</tbody>
</table>
Chapter 4

Studies of cyanide on alkali metal surfaces

4.1 DIET of cyanide on alkali metals and alkali halides

Desorptions induced by electronic transitions (DIET) have been experimentally observed for a variety of diatomic molecules on alkali halide and metal surfaces. Electron-stimulated desorption (ESD) studies of molecules such as NO, O$_2$ and CN on these surfaces have been used to probe the surface-adsorbate bond [20, 57, 58, 59]. In these experiments, the surface was first coated with the adsorbate species. A beam of low-energy (10-300 eV) electrons was directed towards the surface. While these electron energies are too low to cause collision-induced dissociation, desorption can occur through DIET. In ESD through DIET, an inelastic collision between a beam electron and an adsorbate molecule causes an excitation of the adsorbate into an electronic state which is antibonding with respect to the surface. The adsorbate molecule then starts to move away from the surface, and if the excited state lasts long enough, is desorbed. DIET processes are more probable for systems in which rapid quenching of the excitation is unlikely, since if the adsorbate deexcites back into the bonding state before it is far from the surface, desorption will not occur. A wide, continuous valence band such as that present in many metals will cause this rapid quenching. For this reason, systems with no continuous valence band, such as the alkali halides, and systems with a very narrow band, such as alkali metals, are the most likely to exhibit strong DIET effects.

Many ESD experiments have been performed for CN on different alkali halide and alkali metal surfaces [59, 5, 18, 60]. The transition of CN from the $B^2\Sigma^+$ excited electronic state to the $X^2\Sigma^+$ ground state was seen during studies of the desorption of other species such as alkali and halogen atoms from alkali halides. The source of
this cyanide was not immediately obvious, but it has since been proposed that it was formed on the surface from \( \text{CO}_2 \) and \( \text{N}_2 \) that had been adsorbed when the surface was exposed to the atmosphere [18]. The \( \text{CO}_2 \) and \( \text{N}_2 \) molecules were dissociated due to surface effects, and the carbon and nitrogen atoms bonded to form adsorbed CN. The yield of CN has been experimentally observed to increase linearly with the time of exposure to \( \text{CO}_2 \) and \( \text{N}_2 \), in support of this explanation.

### 4.2 Theoretical explanations for the anomalous rotational distribution

We will be discussing the geometries of the adsorbate-surface system in some detail, so it is necessary to first define coordinates. We will define \( \theta \) as the angle between the carbon-nitrogen bond and the surface plane, and \( \phi \) as the angle between the projection of the cyanide bond into the surface plane and an alkali-alkali bond. This is illustrated in Figure 4.1.

Cyanide and other molecules have been observed to have a temperature-independent, non-Boltzmann distribution of rotational quantum states after ESD from alkali halide and alkali metal surfaces [18]. This distribution is independent of electron beam energy and halide species, but varies with different alkali species. Previous attempts to explain this distribution have assumed that the cyanide was bound to a single alkali atom, with the carbon near the surface and clamped in place and the nitrogen able to move as the end of a free or hindered rotor [61]. This explanation has been successfully applied to other adsorbate-metal systems exhibiting similar behavior [20].

One proposed mechanism is that the equilibrium geometry for cyanide in the ground state restricts \( \theta \) rotation to be near the surface normal, and that in the excited state the cyanide is free to move over a much wider range of \( \theta \) [29]. Excited-state electrons are often more mobile than ground state electrons, since they have higher
Figure 4.1 The cyanide-bond / surface-plane angle $\theta$ and the angle between an alkali-alkali bond and the projection of the cyanide bond into the surface plane, $\phi$. 
energies, so it is plausible that a potential barrier to ground-state $\theta$ rotation caused by the Coulomb or Pauli repulsion between the nitrogen electrons and the electrons of adjacent surface atoms would be reduced in an excited electronic state. If the potentials approximate a hindered rotor in the ground state and a free rotor in the excited state, then the rotational eigenstates of these two electronic states will look very different, and any $X^2\Sigma^+$ rotational state will necessarily overlap many of the $B^2\Sigma^+$ rotational states. This overlap will result in significant population of rotationally excited levels in the desorbed cyanide. Any significant difference in rotational potentials between the ground and excited states could cause the observed rotational distribution. The current barrier to the complete understanding of this problem is a lack of reliable potentials for cyanide on alkali halide and alkali metal surfaces.

4.3 Metallization of alkali halide surfaces during ESD

The electron beam in ESD is known to cause the formation of alkali metal islands on an alkali halide surface [3]. This surface metallization has been observed to enhance the yield of desorbed CN [5], but no theoretical explanation of this has been proposed. Rotationally excited cyanide is emitted from both alkali metal and alkali halide surfaces under ESD.

We computed the minimum energy geometries for cyanide bound to clusters approximating the lithium fluoride and lithium metal (100) surfaces. We found that the adsorbate was bound by 1.72 eV on lithium fluoride, and by 5.22 eV on lithium metal. One would therefore expect that lithium metal islands would increase the amount of cyanide bound to the surface, since they are a much more favorable site. This would increase the yield of cyanide from these systems as surface metallization increases, as has been observed. Since the cyanide preferably binds to the lithium metal island
surface sites, we have concentrated much of the rest of our study on that and other alkali metal systems.

### 4.4 The nature of the surface-adsorbate bond

We have performed an exhaustive search of possible bonding sites to find the minimum energy configuration of ground-state cyanide on the lithium fluoride (100) surface. We have also generated potentials for ground- and excited-state cyanide on lithium metal and lithium fluoride surfaces. Before beginning the search for the correct binding site, it was necessary to verify the ability of our method to accurately model the electronic structure of the two components, cyanide and lithium fluoride. We calculated the ground state bond length, vibrational frequency, and anharmonicity of cyanide in the $X^2\Sigma^+$ and $B^2\Sigma^+$ electronic configurations. These results are presented in Table 4.1 along with experimental values. The bond lengths agree with experiment to better

<table>
<thead>
<tr>
<th></th>
<th>$r_e^{LDA}$</th>
<th>$r_e^{exp}$</th>
<th>$\omega_e^{LDA}$</th>
<th>$\omega_e^{exp}$</th>
<th>$\chi_e^{LDA}$</th>
<th>$\omega_e^{LDA}$</th>
<th>$\chi_e^{exp}$</th>
<th>$\omega_e^{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN $X^2\Sigma^+$</td>
<td>1.167</td>
<td>1.17182</td>
<td>2140</td>
<td>2068.59</td>
<td>13.1</td>
<td>13.087</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN $B^2\Sigma^+$</td>
<td>1.145</td>
<td>1.150</td>
<td>2330</td>
<td>2163.90</td>
<td>10.6</td>
<td>20.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

than 1%, and the vibrational frequencies and anharmonicities also agree very well for the $X^2\Sigma^+$ ground state. The excited state anharmonicity is somewhat different from experiment, and the calculated transition energy between the two states is about 1 eV too large. Since density functional theory is only exact for the lowest molecular electronic configuration of each symmetry, these discrepancies between the $B^2\Sigma^+$ result and experiment are not surprising. We do not interpret these differences as
indicating a problem with the experiment, but since our method reproduces the other excited state properties so well, we will cautiously proceed with an investigation of the interaction of cyanide in the $B^2\Sigma^+$ electronic state with various surfaces.

Our implementation of density functional theory is adapted to calculating the electronic structure of finite systems. For this reason, we approximated the (100) lithium fluoride surface in the search for an optimum geometry as a cluster of 18 atoms arranged in a 3x3x2 block, with bond lengths fixed at the bulk lithium fluoride value. This particular cluster has the same stoichiometry as bulk lithium fluoride. Also, this geometry allows the cyanide to be placed in every inequivalent surface position without extending over the edges of the cluster. This property should help minimize cluster size effects, since the four nearest-neighbor surface atoms to the cyanide are always present in the calculation.

The increase in the yield of emitted cyanide with increasing surface metallization implies that the cyanide does not bond to a halogen site. To investigate this, we calculated the binding energies of cyanide in a variety of possible sites on the 18-atom lithium fluoride cluster, and used the more favorable sites as seeds for automated geometry optimization with the methods described in Chapter 2. This procedure explored the entire range of possible binding sites, and should result in an accurate global minimum energy geometry. We find that the lowest energy configuration (Figure 4.2) has the carbon atom not directly over a lithium site as was believed, but rather over a point 1.421 Å along the axis between two lithium atoms, approximately midway between them. The carbon-nitrogen bond is aligned along the lithium-lithium axis, and the bond axis makes an angle of 45.00 degrees with the surface plane. The bond length of the cyanide in the equilibrium configuration is 2.200 Å which agrees with the 2.200 Å bond length that the LDA method gives for free cyanide. Cyanide has a triple bond, so it is not surprising that the bond length is not affected very strongly
Figure 4.2  This is the optimum geometry for the electronic ground state of the cyanide molecule on a lithium fluoride surface represented by a four-atom cluster. Two surface lithium sites and two surface fluorine sites are included. The cyanide almost forms a plane with the two surface lithium atoms. Shown are front, top, and side views, as well as an enlarged front view with perspective.
by the external potential. This geometry has a binding energy of 1.57 eV relative to a separated cyanide molecule and cluster.

The binding energy of cyanide at the previously proposed site, with the carbon directly over a lithium atom, we find to be 0.89 eV, or 0.68 eV less favorable than the binding energy at the optimum geometry. This is a large enough energy difference that the carbon-over-lithium arrangement should not contribute to the desorption process in the ESD experiments that have been performed on these systems. Since our results show that the proposed binding site was incorrect, it is important to examine the rotational potentials with the over-bond-center site, which we will do in Section 4.7. First, we investigate the binding site on a lithium metal surface such as the islands that are thought to form on lithium fluoride surfaces due to electron beam exposure.

4.5 Adsorbate site for cyanide on a lithium metal surface

The metallization of an alkali halide surface causes the formation of alkali metal islands, which effectively have the bulk metal structure. The nearest-neighbor bond length in metallic lithium is 3.490 Å which is close enough to the shortest distance between lithium atoms in lithium fluoride (2.842 Å) that one might expect a similar surface-adsorbate bond. To examine the effects of metallization on the cyanide-surface bonding, we optimized the geometry of cyanide on a lithium metal cluster, using the lithium fluoride optimum geometry as a seed. We found that a local minimum energy was obtained with a geometry very similar to the global minimum energy configuration of cyanide on lithium fluoride. In this case, we represented the (100) surface of lithium metal with a four atom lithium cluster, consisting of two surface atoms and the subsurface atom on either side of the bond. While we have not performed as complete a global search for the optimum geometry of cyanide on lithium metal as
we have on lithium fluoride, the CN-on-lithium potential is considerably simpler due to the presence of only a single species of surface atom, so local potential minima are much less likely. Also, experimental evidence suggests that the bonding is similar for cyanide on lithium fluoride and lithium metal, since the anomalous rotational spectra and the DIET process are seen on both surfaces. We will therefore assume that we have found the global minimum energy configuration of cyanide on lithium metal, which is shown in Figure 4.3, and is very similar to the binding geometry of CN on lithium fluoride.

4.6 Cluster size effects

We calculated the equilibrium geometry of cyanide on a smaller lithium fluoride cluster to verify that cluster edge effects were not significantly affecting our results. These tests were done with a four-atom cluster in a two-by-two square, which also preserves the bulk stoichiometry, and is sufficient to keep a cyanide molecule in the calculated minimum energy state from extending over the edge of the cluster. These clusters are shown in Figure 4.4. We found that the binding energy of CN on this smaller cluster only differed by 0.3 eV from the value with the full 18-atom cluster, and the minimum-energy positions agreed to within 0.1 Å for each atom.

We tested for size effects on lithium metal by adding the next-nearest-neighbor atoms to the central bond, resulting in a 8-atom lithium cluster with the same structure as the cluster shown in the upper right of Figure 4.4. We found that the binding energy of the cyanide on the larger cluster was 5.87 eV (compared to 5.22 eV on the four-atom cluster), and atomic coordinates at the minimum-energy configuration varied by less than 0.05 Å for each atom. This indicates that this smaller cluster is adequate for representing the lithium metal surface near the minimum energy geometry.
Figure 4.3  This is the optimum geometry for the electronic ground state of the cyanide molecule on a lithium metal surface represented by a four-atom cluster. Two surface lithium sites and two subsurface sites are included. The cyanide almost forms a plane with the two surface lithium atoms. Shown are front, top, and side views, as well as an enlarged front view with perspective.
Figure 4.4  Shown are the small and large potassium clusters used to represent the (100) surface of potassium metal (above) and the small and large lithium fluoride clusters used to represent the (100) surface of lithium fluoride (below). The geometries shown in the various clusters here are not drawn to the same scale. The large lithium metal cluster used the same structure as the large potassium cluster, with the correct bond lengths for bulk lithium metal.
We performed the same test for the five-atom potassium cluster we use to represent a potassium metal surface in Section 4.8, and found that increasing the cluster size to 8 atoms changed the binding energy by only 0.27 eV and moved the equilibrium site by 0.3 Å for the carbon and 0.07 Å for nitrogen, which are insignificant on the scale of the 5.22 Å potassium-potassium bond length. These two clusters are also illustrated in Figure 4.4.

4.7 Potential of cyanide on a lithium metal surface

Proposed explanations for the rotational distribution of emitted CN in ESD experiments have depended on significant differences in the ground and excited state rotational potentials. While the exact nature of the excitation that causes the desorption of cyanide from the surface is not known, the emitted cyanide has been observed to undergo to $B^2\Sigma^+$ to $X^2\Sigma^+$ electronic transition. This implies that there is significant overlap between the excited surface state and the $B^2\Sigma^+$ state of free cyanide. This excited state has a single hole in the $2\sigma^*$ orbital and a closed valence shell.

We found that the $2\sigma^*$ orbital of free cyanide did not interact strongly with the surface, and very closely matched an orbital of the combined surface-adsorbate system. This result is reasonable, since we calculate the $2\sigma$ orbital of cyanide to be 36.8 eV above the lithium core orbitals and 12.3 eV below the lithium valence orbitals, so little interaction of the $2\sigma$ cyanide molecular orbital and the surface orbitals is expected. We modeled the combined excited state of cyanide and surface by creating a hole in the cyanide $2\sigma$ orbital and moving that electron up to the LUMO of the same spin. This resulted in an excitation energy of 8.9 eV at the surface.

This excitation energy can be experimentally tested by lowering the kinetic energy of the electrons in an ESD experiment until the cyanide yield drops to zero. At this point, the electrons will be unable to excite the the cyanide into the dissociating state.
While we have not seen this experiment done for lithium, it has been performed for cyanide on a potassium metal surface [58]. We will compare our results for this calculation to the experimental findings in Section 4.8.

One of the requirements for DIET to occur is that the excited state be antibonding with respect to the surface. We generated a potential for the excited state with respect to motion of the CN directly away from the surface, held at the same orientation, which is shown in Figure 4.5 with the ground state potential for the same coordinates. These potentials were generated on a surface represented by the four-atom lithium metal cluster described above. The excited state is clearly much more weakly bound than the ground state. We calculate the excited state to have an equilibrium distance of 1.3 Å and a well depth of only 0.6 eV compared to free $B^2\Sigma^+$ cyanide and the bare surface cluster. Given the potentials in Figure 4.5, and assuming a Franck-Condon transition between states, the excited cyanide is not quite unbound in a purely classical picture. The excited state potential well is so shallow, however, that it is very likely to dissociate.

The Kohn-Sham formalism has been successfully applied to DIET processes in the past [62], but has not previously been used to model desorption processes that result in the anomalous rotational distributions seen in these systems. Theoretical studies using simplified, empirical rotational potentials have shown that with apparently reasonable parameters, the observed rotational distribution of emitted molecules can be reproduced with a hindered-rotor/ free-rotor model as described above [29]. The near-bond-central cyanide binding site should produce a more anisotropic potential for rotation of the CN bond than would a site directly over an alkali atom, since the nitrogen in this configuration will be closer to the neighboring atoms. We examined the $\theta$-rotational potentials of cyanide with carbon clamped. These are plotted in Figure 4.6 for several values of $\phi$ for the $X^2\Sigma^+$ and $B^2\Sigma^+$ states. The ground state potential is a much deeper well than the excited state rotational potential.
Figure 4.5  This illustrates the potential energy surfaces of cyanide in the $X^{2}\Sigma^{+}$ electronic ground state and $B^{2}\Sigma^{+}$ excited state as the carbon-surface distance increases with the orientation and bond length of the molecule held fixed. The solid line indicates the ground state potential, and the dashed line indicates the excited state potential.
Figure 4.6  This illustrates the potential energy surfaces of cyanide in the $X^2\Sigma^+$ electronic ground state and $B^2\Sigma^+$ excited state as the angle $\theta$ (see Figure 4.1) is varied from $0^\circ$, or parallel to the surface, to $90^\circ$, or perpendicular to the surface. The solid line indicates the potential energy value for cyanide in the ground state, and the dashed line for the excited state.
The other requirement for the hindered-rotor model as presented in [29] to be strictly correct is that the carbon be effectively clamped in place. We examined the binding energies of several configurations of cyanide in the same orientation as in the equilibrium geometry, but moved parallel to the surface plane along the lithium-lithium bond and perpendicular to the bond. We found a steep potential well for movement perpendicular to the bond, but a relatively flat potential energy surface for movement along the bond out to distances of at least 0.5 Å, in both the ground and excited electronic states. This indicates that the hindered-rotor model is not a complete description of the potential energy surface. We do find that when the cyanide molecule is in the vicinity of the minimum energy configuration, the ground state wavefunction is more localized in θ than is the excited state wavefunction. This leads us to support the interpretation of [58] for the cause of the anomalous rotational distribution.

4.8 Threshold for DIET of cyanide on potassium metal

Similar rotational effects to those discussed above have been seen in cyanide emitted by DIET processes from potassium metal surfaces. In these experiments, the cyanide yield was observed to drop to zero when the electron beam energy was below 10.88 ± 0.15 eV [58]. This threshold should correspond to the excitation energy of cyanide from the ground to the B²Σ⁺ state when it is adsorbed on a potassium metal surface. Potassium metal has the same crystal structure as lithium, and this result offers another test of our treatment of the adsorbate-surface interaction. We determined a local minimum energy binding site on a five atom potassium structure of four surface atoms and one central subsurface atom for a (100) surface with bulk bond lengths. The equilibrium geometry, which is shown in Figure 4.7, is significantly different from the most favorable lithium site. The cyanide on potassium is
Figure 4.7  This is the optimum geometry for the electronic ground state of the cyanide molecule on a potassium surface represented by a five-atom cluster. Four surface potassium sites and a central subsurface site are included. Shown are front, top, and side views, as well as an enlarged front view with perspective.
coordinated with three surface atoms, rather than two as was seen on lithium. We find that the excitation energy for the cyanide $B^2\Sigma^+$ surface state is 8.8 eV, which is 3.1 eV away from the experimental threshold, shown along with the other threshold calculations in Table 4.2. This may indicate that the excitation energies generated by the LDA for these states are not reliable. The excitation energy for free cyanide also differed significantly from experiment.

**Table 4.2** Threshold energies for DIET desorption of CN on several alkali halide and alkali metal clusters. Energies are given in eV. Present results are indicated by LDA and experimental results by expt when available. Experimental results are for the actual surface which the particular cluster is designed to model. The potassium metal experimental threshold is from [58].

<table>
<thead>
<tr>
<th></th>
<th>$D_e^{LDA}$</th>
<th>$D_e^{expt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_5$</td>
<td>8.8</td>
<td>10.88</td>
</tr>
<tr>
<td>$Li_4$</td>
<td>8.9</td>
<td>-</td>
</tr>
<tr>
<td>$Li_2F_2$</td>
<td>5.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Our method predicts an equivalent cutoff for lithium metal of 8.9 eV, and of 5.1 eV for lithium fluoride. The difference in these two values can be used to experimentally verify the surface binding site as being either a metallized lithium droplet or a lithium fluoride site. While they may not be quantitatively correct, we do predict a significantly lower threshold for lithium fluoride.
Chapter 5

Conclusion

We have examined the electronic structure of alkali halide monomer and dimer clusters, alkali metal dimers, and the $X^2\Sigma^+$ and $B^2\Sigma^+$ states of cyanide in the local density approximation. We have found good agreement between our calculations and experimental results for the geometries and vibrational frequencies of all of the ground state systems. We have then extended these calculations to generate potentials for ground and excited-state cyanide on lithium fluoride and lithium metal (100) surfaces represented by clusters. We found a surprising adsorbate site with the carbon centered between two lithium atoms in both cases. In spite of the unexpected cyanide binding site, the rotational potentials still supported the interpretation that the anomalous rotational population observed in cyanide emitted from these surfaces through DIET was due to significant differences in the rotational potentials between the ground and excited states.

We have also calculated threshold energies for the electronic transition that causes the dissociation, which we found to be in only qualitative agreement with experimental values for a potassium surface. We have predicted these thresholds as a means of distinguishing between the binding of cyanide to lithium fluoride sites and to the lithium metal sites of a metallized lithium fluoride surface.
Bibliography


